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I, JANENE PEISKER, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002952158 for a patent by BHP BILLITON INNOVATION PTY LTD as filed on 18 October 2002.



WITNESS my hand this  
Seventh day of November 2003

JANENE PEISKER  
TEAM LEADER EXAMINATION  
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**PROVISIONAL SPECIFICATION**

**Applicant(s):**

BHP BILLITON INNOVATION PTY LTD  
A.C.N. 008 457 154

**Invention Title:**

PRODUCTION OF TITANIA

The invention is described in the following statement:

PRODUCTION OF TITANIA

The present invention relates to a process for producing titania from a titaniferous material.

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The term "titaniferous" material is understood herein to mean any titanium-containing material, including by way of example ores, ore concentrates, and titaniferous slags.

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The present invention relates particularly to the sulfate process for producing titania from titaniferous material.

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The sulfate process was the first commercial process for the manufacture of titania from titaniferous ores, such as ilmenite.

20

A significant issue with the sulfate process is that it produces large quantities of waste iron sulfate and consumes large quantities of sulfuric acid.

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The chloride process generally avoids the iron sulfate waste problem of the sulfate process and, at larger scales, is less expensive to operate than the sulfate process.

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Hence, the chloride process is the currently preferred process for producing titania, particularly titania for the pigment industry.

An object of the present invention is to provide an improved sulfate process.

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In general terms, the present invention provides a sulfate process for producing titania from a titaniferous material (such as ilmenite) which includes

the steps of:

5 (a) leaching the titaniferous material with sulphuric acid and forming a leach liquor that includes an acidic solution of titanyl sulfate ( $\text{TiOSO}_4$ ) and iron sulfate ( $\text{FeSO}_4$ );

10 (b) separating the leach liquor and a residual solid phase containing titaniferous material;

(c) extracting titanyl sulfate from the leach liquor with a suitable solvent and thereafter stripping titanyl sulfate from the solvent and forming a solution that contains titanyl sulfate;

15 (d) hydrolysing the solution that contains titanyl sulfate and forming hydrated titanium oxides from the titanyl sulfate;

20 (e) separating a solid phase containing hydrated titanium oxides and a liquid phase that are produced in the hydrolysis step (d); and

25 (f) calcining the solid phase and forming titania.

30 The term "hydrated titanium oxides" is understood herein to include, by way of example, compounds that have the formula  $\text{TiO}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{TiO} \cdot \text{H}_2\text{O}$ .

35 In addition, the term "hydrated titanium oxides" is understood herein to include compounds that are described in technical literature as titanium hydroxide ( $\text{Ti}(\text{OH})_4$ ).

The above-described process is characterised by the solvent extraction step (c) of extracting titanyl

sulfate from the leach liquor.

An important advantage of the solvent extraction step (c) is that it does not extract species (such as iron, chromium, manganese, and niobium) that are in solution in the leach liquor that could contaminate downstream products and thereby affect adversely the commercial worth of these products.

In particular, the solvent extraction step makes it possible to produce titania, ie the main downstream product of interest, of very high purity, ie at least 99 wt.%.

Preferably the process includes the steps of precipitating iron sulfate from the leach liquor that is separated from the residual solid phase in step (b) and separating precipitated iron sulfate from the leach liquor.

Preferably the process includes a further leaching step of leaching the residual solid phase containing titaniferous material that is separated from the leach liquor in step (b) with sulphuric acid and forming a further leach liquor that includes an acidic solution of titanyl sulfate and iron sulfate.

Preferably the process includes separating the further leach liquor and a further residual solid phase.

Preferably the process includes supplying the further leach liquor to leaching step (a).

Preferably the further leaching step includes leaching the residual solid phase from step (b) with a raffinate containing sulphuric acid from the solvent extraction step (c).

Preferably the further leaching step includes leaching the residual solid phase from step (b) with the raffinate and make-up fresh sulphuric acid.

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Preferably the raffinate from the solvent extraction step (c) includes at least 250 g/l sulfuric acid.

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Preferably the leach liquor produced in the further leaching step includes at least 500 g/l sulfuric acid.

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More preferably the leach liquor produced in the further leaching step includes at least 600 g/l sulfuric acid.

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More preferably the leach liquor produced in the further leaching step includes at least 700 g/l sulfuric acid.

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Preferably the process includes carrying out the leaching step (a) in the presence of an additive that accelerates the rate of leaching the titaniferous material.

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Preferably the process includes carrying out the further leaching step in the presence of an additive that accelerates the rate of leaching the titaniferous material.

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The use of the leaching accelerant makes it possible to use less concentrated sulphuric acid than is required for the conventional sulfate process.

Preferably the leaching accelerant is selected from the group that includes iron, a thiosulphate salt,

elemental sulphur, sulphur dioxide or any other reduced sulphur containing species.

5 Preferably the process includes carrying out the leaching step (a) in the presence of a reductant that reduces ferric ions to ferrous ions in the acidic solution of titanyl sulfate and iron sulfate produced in the leaching step (a).

10 Preferably the process includes carrying out the further leaching step in the presence of a reductant that reduces ferric ions to ferrous ions in the acidic solution of titanyl sulfate and iron sulfate produced in the leaching step (a).

15 The reductant may be any suitable reductant.

20 Preferably the reductant is selected from the group that includes iron, a thiosulphate salt, elemental sulphur, sulphur dioxide or any other reduced sulphur containing species.

25 As is indicated above, the purpose of the reductant is to minimise the amount of iron in the trivalent ferric form and to maximise the amount of iron in the divalent ferrous form in the leach liquor produced in the leaching step (a) and/or the further leaching step. Maximising the amount of iron in the divalent ferrous form minimises the equilibrium concentrations of iron in the circuit, by promoting the precipitation of ferrous sulphate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .

30 Preferably the leaching step (a) solubilises at least 50% by weight of the titaniferous material supplied to the leaching step.

Preferably the further leaching step solubilises

at least 50% by weight of the titaniferous material supplied to the leaching step.

5            Preferably the solvent extraction step (c) follows the step of separating iron sulfate precipitate from the leach liquor.

10           Preferably the solvent extraction step (c) includes contacting the leach liquor with the selected solvent and a modifier.

            The term "solvent" is understood herein to mean a reagent and a diluent in combination.

15           The term "modifier" is understood herein to mean a chemical which changes the solubilising properties of the solvent such that the titanium containing species are soluble in the solvent at higher concentrations than might otherwise be possible.

20           Preferably the process includes controlling the hydrolysis step (d) to produce a selected particle size distribution of the hydrated titanium oxides product.

25           The controlled growth of coarse particles of hydrated titanium oxides in the hydrolysis step (d) is a significant departure from the conventional sulfate process in which there is a strong preference for producing fine particles in order to produce fine titania  
30           that meets the needs of the pigment industry, the major user of titania.

            There are some applications, such as electrochemical reduction of titania, in which it is  
35           preferable to have a coarse feed of hydrated titanium oxides or a coarse feed of titania.



For these applications, preferably the process includes controlling the hydrolysis step (d) to produce coarse hydrated titanium oxides, ie oxides having a particle size of at least 0.1 mm and more preferably at least 0.3 mm.

Equally, there are other applications, such as production of pigments, in which it is preferable to have a fine feed of hydrated titanium oxides or a fine feed of titania.

For these applications, preferably the process includes controlling the hydrolysis step (d) to produce fine hydrated titanium oxides, ie oxides having a particle size of less than 0.1mm.

Preferably the process includes treating the liquid phase produced in hydrolysis step (d) by neutralising the acid in the liquid phase with lime ( $\text{CaO}$ ) and/or limestone ( $\text{CaCO}_3$ ) and producing clean gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

It is known to produce gypsum by neutralising sulphuric acid in the liquid phase of the hydrolysis step in the conventional sulfate process. However, the gypsum product includes levels of impurities that reduce the market value of the gypsum. The liquid phase produced in hydrolysis step (d) also includes sulphuric acid that can be neutralised to produce gypsum. However, advantageously, this liquid phase is relatively free of contaminants because the solvent extraction step does not extract substantial amounts (if any) of species (such as iron, chromium, manganese, and niobium) that are in solution in the leach liquor that could act as contaminants. Therefore, gypsum produced from this leach liquor is relatively pure.

Alternatively to the preceding step, rather than neutralising the acid in the liquid phase produced in step (e) and producing gypsum, the process may include using the liquid phase as a source of acid in leaching step (a) and/or the further leaching step. Typically, the liquid phase includes of the order of 200 g/l sulphuric acid.

Preferably the process includes calcining the solid phase in step (f) in the presence of a reductant to at least partially reduce the titania.

The calcining step (f) may be carried out in the presence of any suitable reductant, such as hydrogen or carbon monoxide.

Calcination in the presence of the reductant is advantageous because it reduces the amount of energy subsequently required to produce titanium metal (in the event that this is a final product for the calcined product).

Preferably the process includes separating a bleed stream of the leach liquor to minimise the build-up of species (such as iron, vanadium, chromium, manganese, and niobium) in solution in the leach liquor.

The above-described process may be carried out as a continuous process or as a batch process.

Preferably the titaniferous material is ilmenite or naturally altered ilmenite.

According to the present invention there is also provided hydrated titanium oxides that have been produced by leaching a titaniferous material (such as ilmenite) with sulphuric acid and forming a leach liquor that includes an acidic solution of titanyl sulfate and iron

sulfate and thereafter hydrolysing titanyl sulfate and is characterised in that the hydrated titanium oxides include coarse particles of at least 0.1 mm.

5                   The process of the present invention includes the following typical reactions.

Leaching:



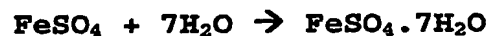
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Ferric reduction:

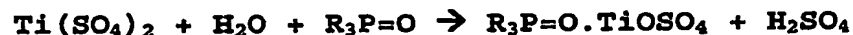


Ferrous sulfate crystallisation:

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Solvent extraction loading:



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Solvent extraction strip:



Hydrolysis:



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Reductive calcination:



30                   The applicant has carried out laboratory scale work in relation to the above-described process.

In summary, the applicant has made the following findings in the laboratory scale work.

35

- Fast leaching rates were achieved by leaching ilmenite in the presence of an accelerant, such as scrap iron, sodium

thiosulphate, and sulphur dioxide.

- Leach liquors containing 100 g/l titanium were produced.

5

- The solvent extraction step resulted in a substantial upgrade in purity of titania that was ultimately produced from the titanyl sulfate extracted in the solvent extraction step.

10

- The liquor stripped from the solvent in the solvent extraction step contained high levels (at least 30 g/l) titanyl sulfate.

15

- Simulated raffinate had sufficient acidity to leach ilmenite in the further leaching step.

- Two stage leaching is an effective leaching option.

20

The laboratory scale work included leaching of samples of heavy mineral sands concentrates containing >50% ilmenite.

25

The leaching work was carried out on a batch basis in 2 stages at atmospheric pressure with 40-60% sulphuric acid at 100-120°C for 3-5 hours in each stage, and with additions of accelerant/reductant in the form of iron, sodium thiosulfate and sulphur dioxide in each stage.

30

The leaching work was carried out with an initial solids loading of 500 g/l.

35

The leaching work was supported by further work using a computer model. This work indicated that a lower initial solids loading of 200 g/l is preferable to the

loading of 500 g/l in the initial laboratory work.

Table 1 is a summary of results of the leaching work.

5 Table 1

Solids loading (in Stage 1)	After Stage 1	After Stage 2
500 g/l	72%	87%
200 g/l	63%	82%

10 Table 1 indicates that 2 stage leaching, under the conditions described above, is an effective leaching step.

15 The laboratory scale work also included solvent extraction tests on leached ilmenite samples using a range of solvent extraction reagents and modifiers, including reagents of the type disclosed in the US patent 5277816 in the name of Solex Research Corporation of Japan.

20 The extraction tests were carried out after crystallisation of excess iron sulfate.

25 The reagents included, by way of example, Cyanex 923 [(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>PO equivalent] and the aliphatic diluent Shellsol D100A. The modifiers included, by way of example, methyl isobutyl ketone (MIBK) and di-isobutyl ketone (DIBK).

30 Table 2 provides the composition of the feed solution and Table 3 provides titanium enrichment factors in the loaded organic.

Table 2

Ti	84 g/l	Ni	28 ppm
Fe	66 g/l	Si	8 ppm
Mn	2.2 g/l	Ca	42 ppm
Cr	87 ppm	Mg	300 ppm
V	270 ppm	Zn	66 ppm

Table 3

	C923	Mix 1	Mix 2	Mix 3	Mix 4
Ti:Fe	275	450	407	909	1636
Ti:Mn	~inf.	~inf.	~inf.	~inf.	~inf.
Ti:Cr	~inf.	~inf.	~inf.	~inf.	~inf.
Ti:V	4.2	6.0	4.1	4.9	6.1
Ti:Ni	1.4	~inf.	~inf.	~inf.	~inf.
Ti:Si	0.14	~inf.	~inf.	~inf.	~inf.
Ti:Ca	~inf.	0.7	0.1	~inf.	~inf.
Ti:Mg	11	~inf.	~inf.	~inf.	~inf.
Ti:Zn	0.3	~inf.	1.4	2.9	1.3
Ti (g/l)	9.1	15.0	14.0	20.0	9.0

5                    Table 2 indicates that solvent extraction, under the conditions described above, is an effective means of separating titanium (in the form of titanyl sulfate) from contaminants.

10                   The solvent extraction tests also indicated that solvent extraction is far more effective if a modifier is present. The modifier did not appear to have any effect on the degree of extraction of titanium. However, the modifier appeared to prevent the formation of an  
15    undesirable titanium-loaded phase that is not soluble in

the diluent. Thus, without the modifier, only relatively dilute solutions of titanium are possible.

5 The improved sulfate process of the present invention is described further with reference to the accompanying flow sheet.

10 With reference to the flow sheet, in a Stage 1 Leach step ilmenite, leach liquor containing 700 g/l sulfuric acid from a Stage 2 Leach step, and a reductant in the form of scrap iron are supplied to a digester 3. The process operates on a continuous basis with the feed materials being supplied continuously to the digester 3 and reacted and unreacted materials being discharged  
15 continuously from the digester 3.

The Stage 1 Leach step solubilises a substantial component of the ilmenite supplied to the digester 3 and produces a leach liquor that contains titanyl sulfate and  
20 iron sulfate. Typically, the leach liquor contains 50-100 g/l titanium and 50-100 g/l iron.

The leach liquor and partially and unreacted ilmenite that are discharged continuously from the  
25 digester 3 are subjected to a solid/liquid separation step.

The solid phase from the s/l separation step, which contains unreacted and partially reacted ilmenite,  
30 is transferred to the Stage 2 Leach step. The Stage 2 Leach step is discussed further below.

The leach liquor from the s/l separation step is transferred via a heat exchanger 5 to an iron sulfate  
35 crystallisation reactor 7.

The heat exchanger 5 cools the leach liquor from

a temperature of the order of 110°C to 50°C. Cooling the leach liquor precipitates iron sulfate from the leach liquor in the iron sulfate crystallisation reactor 7. Typically, the crystallisation step reduces the  
5 concentration of iron in the leach liquor to 40-50 g/l.

The leach liquor containing precipitated iron sulfate that is discharged from the crystallisation reactor 7 is subjected to a further solid/liquid  
10 separation step.

The solid phase from the s/l separation step contains iron sulfate. The solid phase may also contain some species such as iron, vanadium and chromium. The  
15 solid phase is a by-product of the process.

The leach liquor from the s/l separation step is transferred to a solvent extraction reactor 9 and contacts a suitable solvent that extracts titanyl sulfate from the  
20 leach liquor.

Suitable solvents are disclosed in Solex US patent 5277816. The solvents include trioctylphosphine oxide and butyl dibutylphosphonate. The present invention  
25 is not confined to these solvents.

The solvent is used in conjunction with a modifier in the solvent extraction step. Suitable modifiers include MIBK and DIBK.  
30

The solvent/titanyl sulfate mixture is separated from the leach liquor, and thereafter the titanyl sulfate is stripped from the solvent by water.

The recovered solvent is returned to the solvent extraction reactor 9.  
35



The resultant aqueous solution of titanyl sulfate, which typically includes 50-100 g/l titanium in solution and 100-200 g/l sulfuric acid, is transferred to an hydrolysis reactor 11.

5

At start-up, the reactor 11 contains a starting solution of sulfuric acid and solids. Typically, the solution contains 10-200 g/l acid and solids density of 10-200 g/l.

10

The titanyl sulfate solution is added at a controlled rate to the starting solution. The addition of the solution results in the reactor filling up to capacity and thereafter overflowing, whereafter the rate of overflow from the reactor 11 matches the rate of supply of titanyl sulfate solution.

15

In the reactor 11 the sulfate ions in the titanyl sulfate solution are displaced by hydroxyl ions, with the result that hydrated titanium oxides precipitate from the solution.

20

The solids in the starting solution act as seed for precipitation. Typically, the solids are hydrated titanium oxide or titanium dioxide particles.

25

Typically, the residence time of titanyl sulfate solution in the reactor 11 varies between 3 and 12 hours.

30

Subject to temperature and time conditions and control of solution concentration, there is controlled crystal growth in the hydrolysis reactor 11. Controlled crystal growth provides an opportunity to produce titania that ranges from fine to coarse particle sizes. In particular, controlled crystal growth provides an opportunity to produce coarse titania of greater than 0.1 mm which can be used by way of example in the

35

electrochemical reduction of titania to produce titanium. One important parameter for controlling crystal growth is the concentration of titanium in solution. Specifically, it is preferred that the concentration be relatively low,  
5 of the order of 5-10 g/l, to achieve growth rather than nucleation of titanium oxide particles.

The hydrolysis reactor 11 may be operated in batch mode. More preferably, the reactor is operated in  
10 continuous mode.

Moreover, if required, make-up water and solids can be added to the reactor 11.

15 The overflow from the reactor 11 is collected as the product of the reactor 11.

The product from the hydrolysis reactor 11 is subjected to a solid/liquid separation step, which is  
20 facilitated by providing wash water.

The solid phase from the solid/liquid separation step, which contains hydrated titanium oxides, is transferred to a calciner (not shown) and is calcined to  
25 produce titania. Depending on the circumstances, the solid phase may be calcined in the presence of a reductant, such as hydrogen or carbon monoxide, at 1000°C to produce partially reduced titania.

30 In view of the efficiency of the solvent extraction step in confining extraction to titanium compounds, typically, the process produces partially reduced titania of very high purity, ie at least 99 wt.%.

35 The liquid phase from the s/l separation step, which contains sulfuric acid, is neutralised with lime and/or limestone and thereby produces a gypsum product.

In view of the efficiency of the solvent extraction step in confining extraction to titanium compounds, the liquid phase contains minimal levels of contaminants (such as iron, vanadium and chromium) and therefore the gypsum is  
5 "clean" gypsum that is commercially valuable in applications (such as the manufacture of cement). This enables a substantial reduction in waste when compared with the conventional sulfate process.

10               Alternatively, rather than neutralising the acid and producing gypsum, the liquid phase from the s/l step may be reused in the process, for example as a source of acid in the Stage 2 Leach step.

15               The raffinate from the solvent extraction step 9 contains relatively high levels of sulfuric acid (250-700 g/l). The raffinate is transferred to the above-mentioned Stage 2 Leach step and is used as a leach liquor. In  
20 effect, the solvent extraction step recovers sulphuric acid and the acid can be used productively in the process. This enables a substantial reduction in waste when compared with the conventional sulfate process. In  
25 addition, the use of the raffinate as part of the acid feed for the process reduces the amount of fresh acid that is required in the process.

The leach step is carried out in a digester 13.

30               The raffinate, and make-up concentrated sulfuric acid that is also supplied to the digester 13, leach the unreacted and partially reacted ilmenite from the Stage 1 Leach and solubilise approximately 50% of the remaining ilmenite.

35               The product from the Stage 2 Leach is subjected to a solid/liquid separation step.

transferred to the Stage 1 Leach, as mentioned above.

5 The solid phase from the s/l separation step is substantially made up of silicate residue, and is a waste product of the process.

10 Make-up acid is required for the process since there are acid losses in the separation of iron sulfate from the leach liquor and in the extraction of titanyl sulfate in the solvent extraction step.

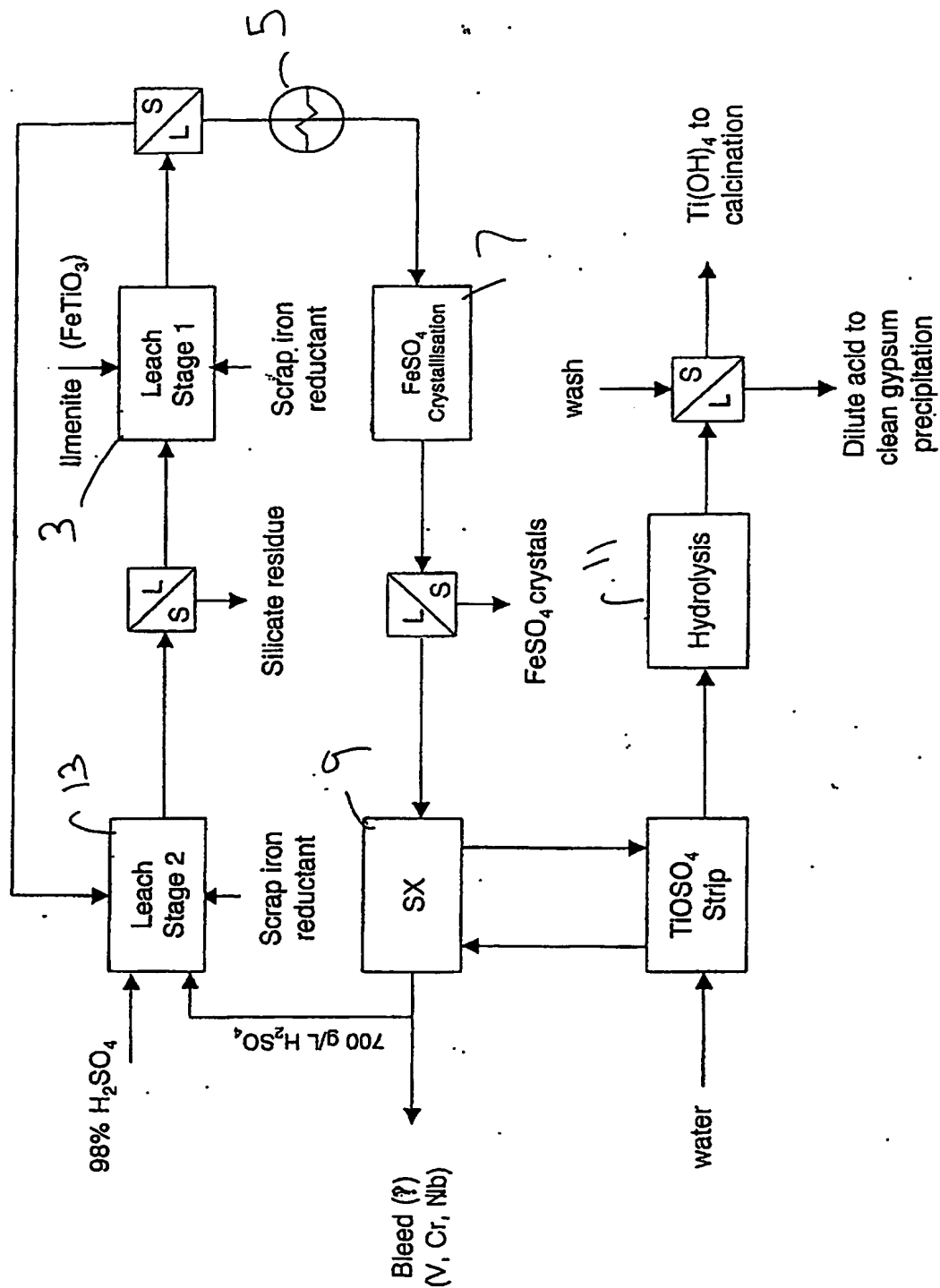
The make-up acid may be added at any point in the flow sheet.

15 The addition of the acid in the Stage 2 Leach step is a preferred addition point because it is thought that the introduction of concentrated acid at this point optimises the opportunity to leach ilmenite, and it is beneficial to maintaining an efficient heat balance.

20 Many modifications may be made to the process of the present invention described above without departing from the spirit and scope of the present invention.

25 By way of example, whilst the Stage 1 and Stage 2 Leach steps have each been described as being carried out in single digesters 3 and 13, respectively, the present invention is not so limited and extends to arrangements that include multiple digesters for each stage.

30 Dated this 18th day of October 2002  
BHP BILLITON INNOVATION PTY LTD  
By their Patent Attorneys  
GRIFFITH HACK  
35 Fellows Institute of Patent and  
Trade Mark Attorneys of Australia



*Possible Reduced Acid Consumption Flowsheet for Ilmenite*